

Predicting coastal variation in surface layer carbon dioxide near Martha's Vineyard MA

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Abstract Data and models addressing variability in ocean surface layer CO₂ partial pressure (pCO₂) near to the coast are examined. The report's main purpose is to instruct aircraft sampling strategies for an air-sea CO₂ flux experiment to take place over the Nantucket Shoals on the Mid-Atlantic Bight. These measurements will be collected in the late summer, providing a seasonal constraint. Review of surface layer carbonate chemistry is given and used to predict probable first-order state variables impacting pCO₂ levels under expected conditions. Forces include along-shore water mass advection (heat and salt flux), surface skin layer heating, biological uptake and respiration, and freshwater flux from the coast. Published observations of coastal surface water CO₂ are surveyed. There has been little data collected on the Mid-Atlantic Bight, but using these data, a generalized model for cross-shelf spatial variability in gas concentration is proposed [DeGrandpre *et al.*, 2001]: pCO₂ variation can be dramatic throughout the seasons within the first 10-20 km from shore with variations spanning from 280 to 550 ppmv [Boehme *et al.*, 1998], in the mid-shelf region this range of variation lessens, and the outer shelf continues this trend – showing swings about equilibrium of less than 40 ppmv. This study also asserts that along-shore variations, at least in a seasonal to annual sense, are minimal and that the simple 1-D cross-shelf model can be applied along the entire continental shelf. The significance of these data and assertions to our region is discussed. The most relevant study presents a multi-year time series pCO₂ analysis [Boehme *et al.*, 1998] along a single cross-shelf sampling transect off the New Jersey coast. This work provides spatial and seasonal detail on measured changes in coastal surface layer carbon. A survey of coastal CO₂ flux experiments in other basins, and of measurements on spatial and temporal pCO₂ variations is made. Key papers are identified and used to bound the time, space and magnitude of pCO₂ variations expected within the experiment domain. Finally, ocean surface biogeochemical models are reviewed to assess their possible role within the proposed field efforts. Issues of boundary conditions, small-scale spatial and temporal resolution, and necessary state variable inputs are examined. Several models are singled out as candidates for further exploration.

1.0 Introduction

The air-sea exchange of carbon dioxide is one central regulating mechanism in the global carbon cycle, where the ocean's surface layer buffers changes in the global atmospheric CO₂ content over time scales of hundreds to thousands of years. Quantifying and monitoring the absolute levels of this gas flux is one goal within efforts to close and understand the global carbon budget and anthropogenic impacts upon it. One aspect of this problem receiving recent attention is air-sea exchange on the ocean continental margins. Carbon cycling is more dynamic near shore due to both abiotic and biotic factors. While these regions comprise only 10% of the ocean's total surface, they account for more than twice this percentage in the total ocean primary production [*Liu et al.*, 2000]. It is postulated that the largest climate change impacts on the ocean carbon system will occur at the coasts due to factors such as river input variability and the future possibility of changes in the overall thermohaline circulation [*Mackenzie et al.*, 2000]. Spatial and temporal scales of variation in surface layer CO₂ partial pressure (pCO₂) are much larger than is observed out to sea [*DeGrandpre et al.*, 2001]. These dynamics lead to sampling and estimation problems when trying to incorporate the coastal ocean into a global carbon budget. They also provide both hurdles and opportunities to the satellite remote sensing community, who propose that some combination of ocean surface wind and temperature and subsurface ocean color data will eventually permit short and long-term global monitoring of the air-sea CO₂ exchange at high spatial resolution.

This summer, a coastal zone field experiment will take place off of Cape Cod that includes the measurement of air-sea CO₂ flux using a low-flying aircraft. The aircraft will collect new data on flux variability at spatial scales of 2-50 km, this over a fairly dynamic oceanic region that includes the biologically-active Nantucket Shoals. These data can be used to assess CO₂ flux remote sensing applicability in coastal margins. Flux variation will often be driven by changes in the ocean surface layer pCO₂. However, this key variable will only be measured on a limited basis using shipboard and tower sampling, and not by the aircraft. This report attempts to anticipate the mean levels and time/space pCO₂ variability including a look at the likely controlling processes. The

approach taken is to review available data, literature, and biogeochemical models relevant to this study site. Results can then be used to devise aircraft sampling strategies that minimize and maximize in-water pCO₂ impact on observed CO₂ fluxes.

2.0 Background

The Office of Naval Research is sponsoring a program to look at Coupled Boundary Layers and Air-Sea Transfer (CBLAST). One program component addresses interfacial processes that control heat, moisture and momentum flux under light wind conditions. This objective is being undertaken using field and model efforts centered on an observation site off of Martha's Vineyard as shown in Fig. 1. The extent of this map is roughly 40 x 40 km. A measurement platform within this experiment is the NOAA's LongEZ research aircraft (N3R). This plane is outfitted to measure CO₂ flux using the eddy correlation method using fast (IRGA) and slow-rate (LI-COR 6262) CO₂ sensors alongside wind turbulence measurements as shown in Fig. 2. Daily aircraft data collection will take place in August of 2002 and 2003 and will coincide with surface truth at fixed moorings, the dedicated flux tower (ASITower), and limited ship-board data collection.

One objective for the aircraft program is to assess the remote sensing of CO₂ flux for this dynamic coastal region. Recall that the mass flux equation approximating CO₂ air-sea exchange, F , is [Wanninkhof and McGillis, 1999]:

$$F = k_w * S * (pCO_{2_air} - pCO_{2_sea}) \quad (1)$$

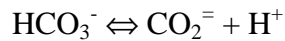
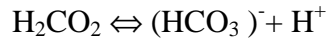
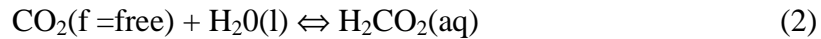
where k_w is an empirically determined gas transfer coefficient, and S is a well-defined solubility constant for CO₂ in seawater – a strong function of the water temperature. The aircraft will be able to measure or model S , F , and pCO_{2_air} to known levels of accuracy. The parameter k_w is nominally defined as a function of the near-surface wind speed (references) and is the subject of active research [Bates and Merlivat, 2001; Tans *et al.*, 1990; Wanninkhof, 1992; Wanninkhof and McGillis, 1999]. Still, we will also be

measuring the wind speed and its variability quite accurately, thus k_w can also be estimated. This leaves the possibility to solve Eq. 1 for pCO_{2_sea} concentration and its variation along the flight track.

Predicted accuracy in such a pCO_2 inversion is certainly not at the 1 μatm level obtainable using direct measurement techniques. Optimistic estimates give an rms uncertainty of 20-30 μatm for the case where repeated transects are flown to limit flux estimate errors. Along-track spatial resolution is set by the eddy correlation flux technique to extents of greater than 1-2 km. So a few key questions arise. What is the expected range of variation for surface layer pCO_2 levels about this coastal region? Does this concentration vary strongly over scales below 1-2 km or at times less than 10-20 minutes? Is there a predictable set of processes controlling pCO_2 dynamics here?

3.0 CO_2 surface layer chemistry

An initial inquiry into what to expect can be obtained by review of inorganic carbon chemistry in seawater [Millero, 1996; Pilsen, 1998]. The equilibrium reaction of CO_2 placed in contact with seawater falls under the acid-base classification, i.e. proton exchange. Carbonic acid (H_2CO_2) is the weak acid formed when CO_2 contacts water, and is buffered by seawater in the following three reactions:



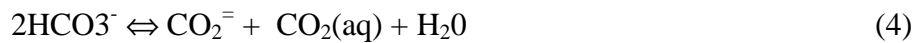
Total CO_2 (TCO_2 or dissolved inorganic carbon (DIC)) is the combination of the following species:

$$[TCO_2] = [CO_2(aq)] + [(HCO_3)^-] + [CO_2^{=}] \quad (3)$$

The concentration of dissolved, or aqueous, CO₂ is not easily measured. In practice, its activity is estimated by measuring pCO₂ and then applying Henry's law along with the known CO₂ solubility factor (H_{CO2}) for seawater.

The complete CO₂ system, including pH and the partial pressure of CO₂ within solution, is described by specifying at least two of three parameters [TCO₂, pH, pCO₂] [*Pilsen*, 1998]. Estimates for each reaction's apparent dissociation constants (in seawater) are also required, along with the water temperature, salinity and pressure. The composite equation defining pCO₂ can take numerous forms, depending on the measurements made and the empirically-derived system constants chosen [*Wanninkhof et al.*, 1999].

Complete details for this CO₂ buffering system and its measurement are rather complex and not presented here (see [*Pilsen*, 1998]). However, there are a few central points that may help clarify where free CO₂ fits within seawater DIC. First, DIC is dominated by bicarbonate ion in the ocean. Typically, it comprises more than 90% of DIC, with carbonate providing 9% and free CO₂ (i.e. pCO₂) carrying only 1% of the pool. The net reaction maintaining balance amongst these species can be written as:



That is, the bicarbonate component of the TCO₂ pool is either built up or depleted to satisfy LeChatelier's principle in accord with any modification to either free CO₂ or carbonate concentrations. Implicitly, this net reaction conserves pH. The net rate of reaction in seawater is on the order of minutes, thus the large bicarbonate pool is a central player in buffering change in the other species.

Finally, water temperature and salinity are dependent variables in both the dissociation and solubility constants mentioned above. This fact, along with nonlinear covariance between the three species (and pH), complicates single parameter sensitivity analyses – e.g. predicting the effect of temperature change on pCO₂. Exact pCO₂ variation modeling

requires specifying initial TCO_2 (or initial pCO_2), temperature, salinity and alkalinity (see below).

3.1 Main perturbation factors for coastal surface layer pCO_2

The gas flux objectives defined above set the focus on CO_2 partial pressure in the coastal ocean surface layer. When and why does near-surface pCO_2 vary within this system? The following discussion is limited to non-estuarine coastal waters in August, time scales of days to weeks, and assumes no deep-ocean upwelling input.

An obvious factor is CO_2 gas flux at the air-sea interface. Equilibration with the atmosphere should modify $\text{CO}_2(\text{aq})$ when in-water pCO_2 does not match the atmospheric level. But it turns out that this exchange is typically slow except in very shallow water (low surface layer volume) or for high wind speeds [*DeGrandpre et al.*, 1997]. This factor is considered as second-order for study at the day to month time scale except very near the coast.

A first-order factor controlling pCO_2 variation is change in water temperature. CO_2 is a relatively soluble gas and the solubility varies strongly with temperature. As water with a given $[\text{CO}_2(\text{aq})]$ warms, Henry's law dictates that pCO_2 must go up. This often leads to pCO_2 super-saturation in the summer until vertical water mass mixing or air-sea exchange can draw this down. An additional aspect to solubility, especially in the summer, is the fact that the surface skin temperature can often depart from the bulk surface layer temperature (e.g. as measured by ships at 2-3 m depth) by as much as degrees $^{\circ}\text{C}$ due to surface solar input and weak mixing. Air-sea gas transfer takes place across the skin and thus it is the in-water pCO_2 level right in this $O(\mu\text{m})$ skin layer that matters [*McNeil and Merlivat*, 1996]. This is perhaps a second order issue, but one that matters most in the summer and where the skin-to-bulk temperature difference is spatially variable. Along- and cross-shelf water mass advection, wind mixing, and strong solar forcing are all expected to contribute to temperature variability during the experiment.

Another first-order $p\text{CO}_2$ perturbation comes from DIC flux. For a fixed water temperature and salinity, $\text{CO}_2(\text{aq})$, and hence $p\text{CO}_2$, varies almost directly with DIC. Large swings in $p\text{CO}_2$ will accompany small changes in total carbon. A key DIC modifier in coastal waters is water mass mixing of differing carbon pools due to local upwelling, tidal-front mixing, and freshwater or along-shore fluxes.

These physically-driven perturbations are augmented by biological carbon cycle modifications in surface waters, especially in the event of advected nutrients. This includes heterotrophic remineralization of carbon within the surface layer, where DOC is respired to raise DIC levels. On the sink side there will be $[\text{CO}_2(\text{aq})]$ drawdown due to photosynthetic uptake. The presence of biology will most likely be spatially variable and temporally episodic in this region, as it is primarily dependent on nutrient delivery water column mixing rates. More discussion on biological forcing comes in the following sections, but note that the first-order variables needed to characterize these processes would be chlorophyll a (i.e. biomass), nitrate (NO_3^-), and dissolved oxygen concentrations.

Finally, change in the total or carbonate alkalinity ($\text{TA} \approx \text{CA} = \text{HCO}_3^- + \text{CO}_3^{2-}$) may also alter $p\text{CO}_2$ under certain conditions. CA perturbation is largely associated with fluctuations in CaCO_3 concentration. Calcium ion is a nearly unlimited constituent in the sea. Calcium carbonate is built into the exoskeleton of certain phyto- and zooplankton species that live, die and decompose in the surface ocean. The eventual surface-layer export or dissolution of particulate CaCO_3 depends on salinity and acidity (pH). These are the 1st order factors perturbing total CA, and hence $p\text{CO}_2$. CA and pH are often coastally covariant in absence of strong biological activity where an increasing seaward salinity gradient drives CA upward (pH as well). That is, when more negative charge is needed to balance the cations present (say an increase in Ca^{2+} due to upward salinity), then the carbonate system converts HCO_3^- to CO_3^{2-} , thereby making more negative charge (CO_3^{2-} has two neg. charges, whereas HCO_3^- has only one). An empirical relationship between TA and seawater salinity for a given region of the ocean or coast is often derived

that tries to approximate the overall biotic and abiotic character such that the more common salinity measurement can be used to prescribe TA.

3.2 Magnitude of pCO₂ variation

This brief overview suggests that SST, DIC, and salinity (or TA) are the primary physical and chemical state variables needed to study pCO₂ variation. A measure of pH would also be helpful. Some sense for the expected order of magnitude in pCO₂ variation is given in Table 1. Field measurements were augmented, where necessary, by CO₂ system calculations. Several complete seawater CO₂ chemistry calculation programs are publicly available. These programs generally follow DOE protocols [*Dickson and Goyet, 1994*] and we chose a model ([http://neon.otago.ac.nz/chemistry/research/KAH/software/swCO₂.htm](http://neon.otago.ac.nz/chemistry/research/KAH/software/swCO2.htm)) that permits pCO₂ sensitivity estimates by variation of inputs. Note that no estimate for biological alteration of the system is listed here. This factor is not simply modeled, but is assessed empirically below.

What should be apparent in Table 1 is that there are factor of two swings in surface layer pCO₂. These are much more dramatic than for DIC or TA. It is clear in Fig. 3 that DIC or SST can drive large pCO₂ swings with all other variables fixed. The decoupling to a single dependent variable is not completely realistic and so the sensitivity and extent of the pCO₂ variation is probably too strong in the figure. However, as shown in the following section, pCO₂ variation in the coastal region does vary over the large ranges shown in Fig. 2 in response to some combination of these controlling processes.

A more comprehensive list of measurement variables, the level of CO₂ perturbation, and controlling processes is provided in Table 2.

4.0 Observations of coastal pCO₂ variation and of the CBLAST region

The discussion above suggests that physical, chemical and biological factors may all play some role in modifying pCO₂ in our study area. This section presents a literature review where the main search criteria are 1) near-shore measurements of the CO₂ system, 2) small spatial or temporal scale variation in surface layer pCO₂, or 3) physical and biological oceanographic studies conducted near the Nantucket shoals area. The studies are then used to discuss spatial and temporal variation in surface layer carbon within the constraints of the upcoming study. *A priori* constraints include:

- August-September
- Daytime sampling due to aircraft
- Spatial sampling from the beach out to 100 km in any direction from Martha's Vineyard
- Shallow water (< 20-40 m) with little direct deep-ocean water intrusion

4.1 CBLAST region hydrography and biology

Documentation of oceanographic characteristics near to the Nantucket Shoals and Martha's Vineyard is needed in order to gain perspective on dominant controlling processes and to develop sampling strategies. There are not many recent studies of this region but the area was characterized from the 1920s-1970s [*Beardsley et al.*, 1985; *Bigelow*, 1927; *Limeburner and Beardsley*, 1982]. Several recent remote sensing climatologies have produced both biology and sea surface temperature signatures [e.g. *Yoder et al.*, 2001]. Moreover, OMP program pCO₂ data, expected physical data to come from the experiment itself, combined with several past sampling efforts nearby, [*Campbell et al.*, 1986; *Ramp et al.*, 1988; *Subramaniam et al.*, 1999; *Wainwright and Fry*, 1994] do provide a measurement basis to work from. A comprehensive model for the larger region [*Chen et al.*, 2001; *Franks and Chen*, 2001] encapsulates much of this water column information and provides a sense of prevailing conditions which add additional constraint to the present pCO₂ survey:

Off shore (SW of MV, and > 20 km from shore)

- Warm and nearly well mixed, only a weakly stratified vertical profile (see CBLAST WHOI/AOP data)
- Low biological productivity (SeaWiFS catalogue)
- High variability in skin layer SST under light winds (pers. comm., C. Zappa)
- Small horizontal gradients in salinity and bulk temperature
- Prevailing along-shore current towards south
- Episodic biology in response to water mass advection from NE

Near shore (S/SW of MV and < 20 km from shore)

- Well mixed water column due to high tidal mixing
- High SST, variation dependent on long-term currents
- Cross-shore salinity gradient of 0.5 psu over 10-20 km
- Higher level of photosynthesis; chronic; diurnal
- Possible nutrient flux from large NE Cape Cod source

Nantucket shoals

- Prevailing CW surface current around Nantucket Island
- Well mixed; relatively high turbidity
- Relatively low SST due to tidal front mixing and entrained GOM water
- High nutrient (nitrate) flux from the bottom, Cape Cod and GOM
- Higher level of photosynthesis; chronic; diurnal

Some of these aspects are captured in Figs. 4, 5 and 8 which show a sample satellite-derived chlorophyll A (Chl_a (mg/m^3) \sim measure of autotrophic biomass) and sea surface temperature (SST) maps. One finds more productivity near the coast than out to sea. The Nantucket Shoals is an off shore exception where the chronic tidal stirring over the shallow depths permits steady, seasonally-invariant productivity. Overall productivity observed suggests substantial nutrient input and physical advection that are not necessarily predicted for this time of the summer, but that certainly make for a biologically diverse environment. This may bode well for large magnitude, well-defined spatial pCO_2 gradients. The same can be said for the SST variations present in Fig. 5.

4.2 Observed pCO₂ variability

Papers examining near-shore pCO₂ variation address both biological and physical forcing [Alvarez *et al.*, 1999; Boehme *et al.*, 1998; Borges and Frankignoulle, 1999; Crawford *et al.*, 1993; Currie and Hunter, 1999; DeGrandpre *et al.*, 1998; Frankignoulle and Borges, 2001; Frankignoulle *et al.*, 1996; Hood *et al.*, 2001; Liu *et al.*, 2000; Murphy *et al.*, 2001b; Perez *et al.*, 2001; van Geen *et al.*, 2000; Veldhuis *et al.*, 1994; Zirino *et al.*, 1997]. The list is not long and is weighted towards studies of coastal upwelling events common to the eastern boundaries of the Atlantic or Pacific. These latter cases are not directly relevant to the CBLAST measurement site as they represent large deep-ocean DIC and SST modifications of surface waters, and large biological production. The studies with most direct relevance here were conducted on the U.S. east coast [Boehme *et al.*, 1998; DeGrandpre *et al.*, 2001; Takahashi *et al.*, 2001]. A program of particular import was the Oceans Margins Program (OMP) conducted in the mid-1990s under JGOFS (<http://www.oasdp.bnl.gov/mosaic/omp/>).

Numerous papers address spatial and temporal variation of pCO₂ in the open ocean; too many to list here. Restricting the list to those that address variation at our short time and length scales leads to a smaller group (exclusive from the list above) [Bakker *et al.*, 1997; Bakker *et al.*, 2001; Barbosa *et al.*, 2001; Bates *et al.*, 1998; DeGrandpre *et al.*, 1997; Fraga *et al.*, 1999; Hood *et al.*, 2001; Keir *et al.*, 2001; Martin *et al.*, 2001; Metzl *et al.*, 1995; Murphy *et al.*, 1998; Murphy *et al.*, 2001a; Wanninkhof *et al.*, 1993].

There has been little CO₂ data collected on the Mid-Atlantic Bight, but using these data, a generalized model for cross-shelf spatial variability in gas concentration is proposed [DeGrandpre *et al.*, 2001]: pCO₂ variation can be dramatic throughout the seasons within the first 10-20 km from shore with variations spanning from 280 to 550 ppmv [Boehme *et al.*, 1998], in the mid-shelf region this range of variation lessens, and the outer shelf continues this trend – showing swings about equilibrium of less than 40 ppmv. This study also asserts that along-shore variations, at least in a seasonal to annual sense,

are minimal and that the simple 1-D cross-shelf model can be applied along the entire continental shelf. This is a key hypothesis that the CBLAST data set may support or weaken.

DeGrandpre's observations and discussion regarding near shore $p\text{CO}_2$ variation draw extensively from a multi-year time series $p\text{CO}_2$ analysis [Boehme *et al.*, 1998] along a single cross-shelf sampling transect off the New Jersey coast. This work provides spatial and seasonal detail on measured changes in coastal surface layer carbon. For example, Figure 6 is taken from this study to demonstrate that $p\text{CO}_2$ (note that CO_2 fugacity ($f\text{CO}_2$) is nearly identical to $p\text{CO}_2$) is most variable nearest to the coast and to show the large swings that are observed. Boehme *et al.* provide comprehensive discussion of the carbonate perturbing forces during their study. In the summer, the processes driving variation at day-to-week and km scales were:

- Temperature (heat flux) ; advected/upwelling water drives $p\text{CO}_2 \pm 150 \mu\text{atm}$
- Biology; diurnal, stronger and more episodic near shore ($< 5 \text{ km}$); $p\text{CO}_2$ variance of $\pm 80 \mu\text{atm}$; respiration and uptake
- Persistent cross-shore salinity+DIC gradients; increase of 0.5 psu away from shore accompanied by DIC drop, drives $p\text{CO}_2$ down by 20-30 μatm

These general findings fit well with another recent study in coastal waters [Currie and Hunter, 1999].

Data from the OMP program [Takahashi *et al.*, 2001] collected just to W and SW of the CBLAST site are shown in Figure 7. The observations show a span in $p\text{CO}_2$ from 220 to 450 μatm and hint at the covariance between $p\text{CO}_2$ and SST. Salinity and temperature were nearly correlated so that it is not immediately apparent which factor may be controlling the carbon variations, but as seen in Fig. 3, the trends seen in the present data suggest that the primary control is SST. This is because the salinity increase should drive a $p\text{CO}_2$ decrease. The scatter in the middle panels is a likely indicator of the control complexity that actually exists.

Three central conclusions were drawn from this review. First, Boehme et al. provides a guide for how to sample and study the complete pCO₂ system and its variance. Second, it is apparent that the CBLAST region (in August) should encompass a range of surface water pCO₂ levels both in space and time. Crude zonal prediction is given in Fig. 8. Table 1 incorporates the limited observations, and estimates others, to bracket the state variable magnitudes and pCO₂ changes. Finally, resolving pCO₂ controls in this region would be a complex task. Satellite or aircraft SST and ocean color data alone will provide only partial information needed to sort out when and why the pCO₂ levels change. Still, it is clear that SST will be of first-order importance. This is the case for most investigations that were reviewed.

5.0 Ocean biogeochemical models and pCO₂ variation

Can an ocean model predict the surface water carbon levels for this measurement site? To answer this question, a survey was made of ocean biogeochemical models and how they resolve spatial and temporal evolution of surface layer pCO₂. The list of investigators and efforts within this topic is extensive. Models span from simple 1-D box models that deal only with the physical ocean circulation (i.e. the heat driven solubility pump, [Sarmiento et al., 1992]) to 4-D fully coupled biogeochemical-physical global predictions that predict complete net ecosystem exchange [Spitz et al., 2001]. There is clear evolution within this community towards a point where physical and biological forces can now be mutually addressed, but also to where a model's level of complexity should be driven by the task at hand [Doney, 1999; Fennel and Neumann, 2001; Moore et al., 2002]. Not unexpectedly, no model studies have focused on the local Cape Cod region and its pCO₂ variation on short space and time scales. Discussions with several investigators active in this field led to a refocus for this survey. In their opinion, the task of defining, updating, and incorporating physical and chemical boundary conditions into a robust physical-chemical model for this coastal region is a daunting, but necessary task. Much of the literature in this type of ocean modeling deals primarily with vertical mixing on the open ocean using box models. The MV site is almost opposite to this case, where all flux is advective. Given this guidance, the following discussion only sketches out the

tools and preconditions needed for an intermediate complexity model that would capture the larger aspects of the surface layer $p\text{CO}_2$ that are identified in Figure 8.

Based on the groundwork provided above, both biological and physical factors will perturb the surface layer chemistry during the CBLAST (MV) experiment. In addition, three locally-coherent physical zones were identified, the Nantucket Shoals (NS), the low productivity region directly to the SW (the “deep water” CBLAST region), and the cross-shore coastal gradient from MV out to this deep water area. So, it is proposed that several single layer box models could be developed. For example, one could envision independent time-series models for surface layer $p\text{CO}_2$ in the two boxes depicted in Figure 8 where the temporal covariance and spatial gradients between these boxes could be then measured for validation.

In all cases one can consider the vertical structure to be nearly isothermal and the ocean bottom as one vertical boundary condition. The flux into and out of these boxes would occur in the horizontal with a known prevailing W/SW current derived from the eastern flank of the NS. Strong M_2 tidal stirring is present, especially near NS. While much of the physical data necessary to model these boxes should be available from the measurement complement (ships, buoys, aircraft, satellites), it will likely be necessary to develop some means of sampling DIC or DIN across this region, perhaps in conjunction with DO. Clearly, it is the horizontal (advective) flux of nutrients, heat, and DIC that will provide the hurdle for developing such a model.

Several studies have been identified as amenable or relevant to the processes, location, and data available for such a study. These include the following [*Antoine and Morel*, 1995a; *Antoine and Morel*, 1995b; *Chen et al.*, 2001; *Franks and Chen*, 2001; *Mahadevan and Archer*, 2000; *Moisan and Hofmann*, 1996; *Moore et al.*, 2002; *Signorini et al.*, 2001; *Signorini et al.*, 2002]. The model of Antoine and Morel is the most directly applicable to remote sensing data assimilation but is a 1-D open ocean model, thus the vertical diffusion would need to be replaced with developments to handle the horizontal exchange. The model of Franks and Chen (2001) shows the most promise as it already

incorporates most of the local oceanic dynamics, including biological and physical coupling over the Nantucket Shoals. This effort is not strong in the chemical aspect, but modification along the lines of Signorini et al. (2001) would bring in the requisite $p\text{CO}_2$ emphasis.

Finally, search of the literature and web sites did dig up several sites where executable box models for the carbon system are available. These include:

- Doney - <http://www.cgd.ucar.edu/oce/doney/bats/bats.html>
- Sharples - http://www.so.es.soton.ac.uk/staff/js/phyto_1d.html
- Gnanadesikan - <http://www.gfdl.noaa.gov/~a1g/MAE554/ocean.html>

6.0 Conclusions

This study provides a general overview of the issues surrounding where, why and how $p\text{CO}_2$ levels will vary over the CBLAST region during the summer experiments. Space/time prediction of carbon levels is not possible because such local observations of $p\text{CO}_2$ and the carbonate system are not available. These would be required to improve upon the broad range of levels provided in Table 1. Studies relevant to the local hydrography, biology and chemistry of this region are listed in the text. Boehme et al. (1998) provides a good case study of cross-shore $p\text{CO}_2$ perturbations along a 30 km transect that includes some resolution of controlling processes. Though not directly applicable to the coming aircraft spatial sampling work, they do provide a water sampling and process analysis framework that could be adopted in many respects. Numerous studies and data sets are drawn upon to suggest that there may substantial (~ 50 - $100 \mu\text{atm}$) along and cross-shore gradients in surface water $p\text{CO}_2$ over length scales of 5-20 km, as well as short time and spatial scale forcings. Details are summarized in Tables 1 and 2 and Figure 8.

An end objective for this work is development of a water and aircraft sampling plan that leads to resolution of $p\text{CO}_2$ gradients exceeding $\sim 30 \mu\text{atm}$ per 20 km via eq. 1. This plan will not be described here but several tasks that remain in support of the planning are:

- Catalogue Aug. AVHRR SST images for 1997-2001 at 3 day intervals
- Catalogue all clear day Aug. SeaWiFS images for 1998-2001
- Summarize NOAA Nan98 Chl_a data and accessory pigments
- Decide which process/gradient to place focus on in 2002
- Develop realistic water sampling protocol for 2002 ships of opportunity
- Address diurnal time scale issue in the sampling
- Look at fog and cloud cover stats for Nantucket Shoals

Table 1: Estimates of variable limits for the coastal waters near to Martha's Vineyard MA. Measurement or estimate sources are included in the notes on the right.

| Variable | Low value | Median Value | High Value | Notes |
|--------------------------|-----------|--------------|------------|--|
| SST (C) | 15 | 21 | 27 | CBLAST buoy, AVHRR |
| Salinity (psu) | 30.5 | 31.2 | 31.5 | CBLAST buoy |
| DIC (ug/m ₂) | 1850 | 1920 | 1950 | OMP-deep:1900-1950; CO ₂ sys-est: 1850-1950, TA locked to SSS |
| pCO ₂ (µatm) | 215 | 267 | 600 | CO ₂ sys computed; Boehme98:280-450; OMP6-10/96: 240-450 |
| TA | 2112 | | 3159 | CO ₂ sys S-to-TA; TA seems high for OMP |
| Phosphate | 0.1 | 0.4 | 0.5 | Boehme98: August |
| pH | ? | ? | ? | |
| | | | | |
| Atm_pCO ₂ | 270 | 275 | 400 | CBLAST- MVCO |

Table 2: Some pCO₂ perturbing processes expected during CBLAST along with general level of variation and the spatial and time scales anticipated. Latter factors are derived from the literature search, Table 1, and map of the dynamics (Fig. 8). Dependent variables are those that will likely correlate with observed carbon system dynamics.

| Process | Dependent Variable(s) | ΔpCO_{2_sea} (µatm) | 1/e time scale (day) | 1/3 space scale (km) | Diurnal cycle? |
|---|--|------------------------------|----------------------|----------------------|----------------|
| Surface heating; skin effect | SST and bulk water T | +20-60 | 0.05-0.2 | 0.01-0.5 | |
| Biology; Respire/Photosyn. | Chl _a , PAR, DO, DOC, NO ₃ | +/-100 | 0.3-10 | 1-10 | yes |
| Water mass advection; salt,heat,nutrients | SST, salinity, NO ₃ | -100,+200 | 1-5 | 1-20 | no |
| Coastal cross-shore gradient | Salinity,DIC?, Chl _a ,NO ₃ | 20-50 | N/a | 10 | no |
| Nan. Shoals gradient (see Fig. 8) | SST, DIC, Chl _a ,NO ₃ | >200? | N/a | 2-10 | Weak? |

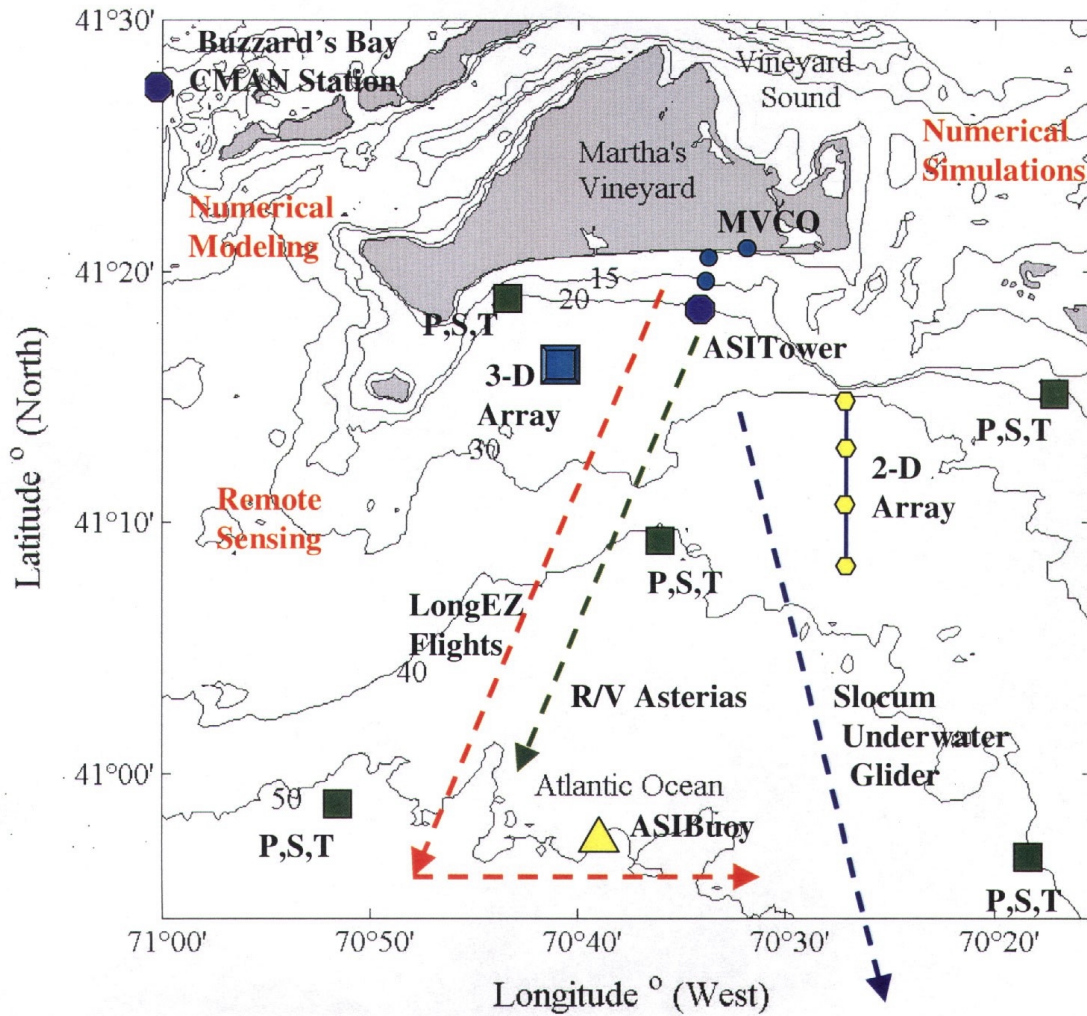


Fig. 1: The ONR CBLAST measurement region (roughly 40 km x 40 km) including the location of the central measurement tower (ASITower) and buoys. The aircraft is able to sample over any portion of this region numerous times within a given day's flight.

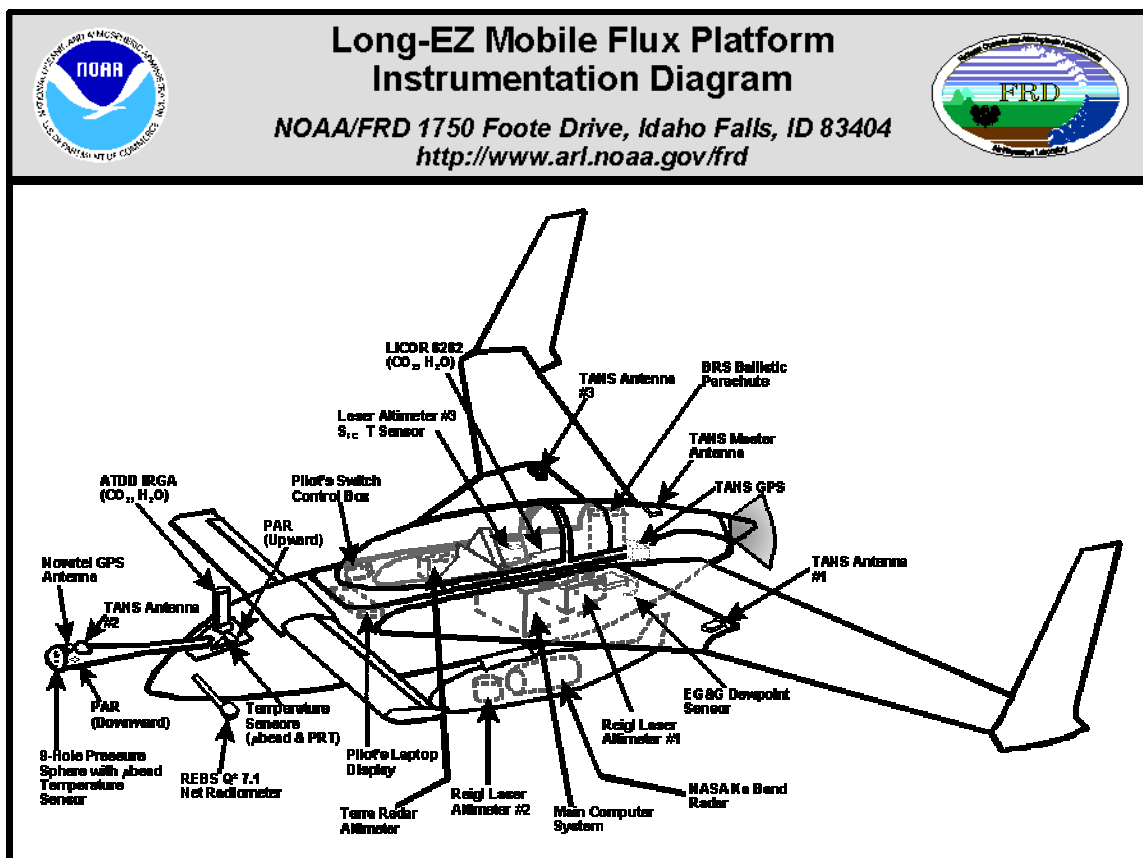


Fig. 2: LongEZ (N3R) research aircraft. This aircraft will be used to measure or estimate all parameters in Eqn. 1 except the surface water pCO_2 . CO_2 flux is estimated using the eddy correlation technique over spatial scales of 1-5 km. SST, wind, and surface waves are measured using the aircraft as well.

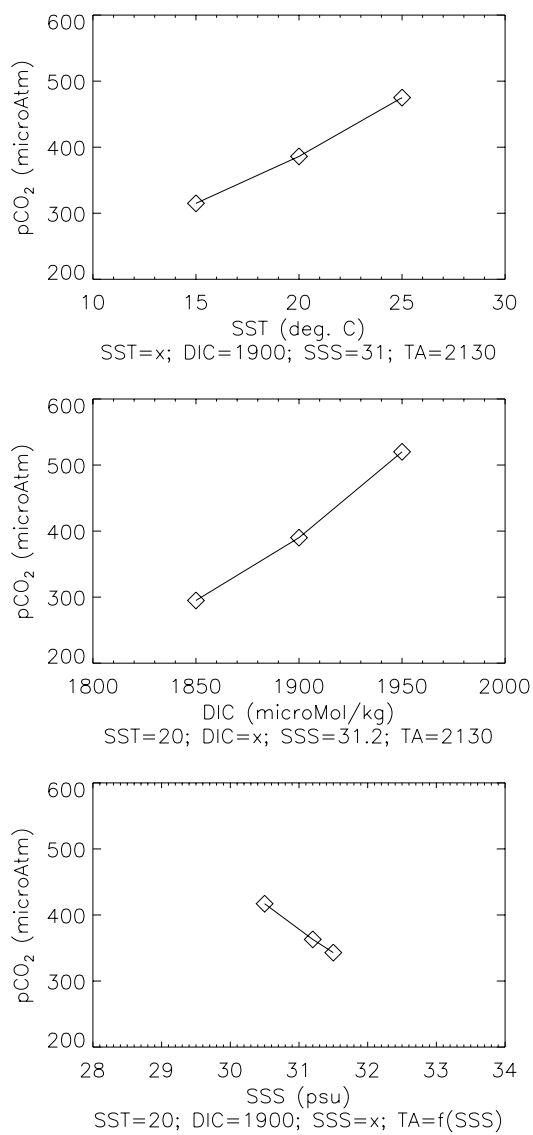


Fig. 3: Estimates of seawater $p\text{CO}_2$ for expected variations, see Table 1, in a) SST, b) DIC, or c) TA. The other dependent systems variables are fixed as noted. Computations are made using CO2sys.exe.

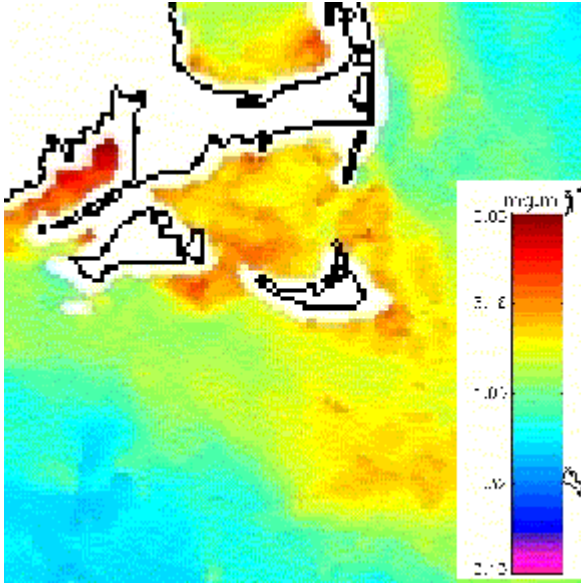


Fig. 4: Expanded view of the experiment region. Color code represents Chl a concentration (biomass) as derived from an 8-day average of SeaWiFS satellite images in August 2001. Note the highest (red) levels appear nearest to the coast but that high levels also appear south of Nantucket Island (the island situated farthest south on this map). Finally, the blue region to the southeast represents nutrient-depleted water typical of off-shore conditions this time of year.

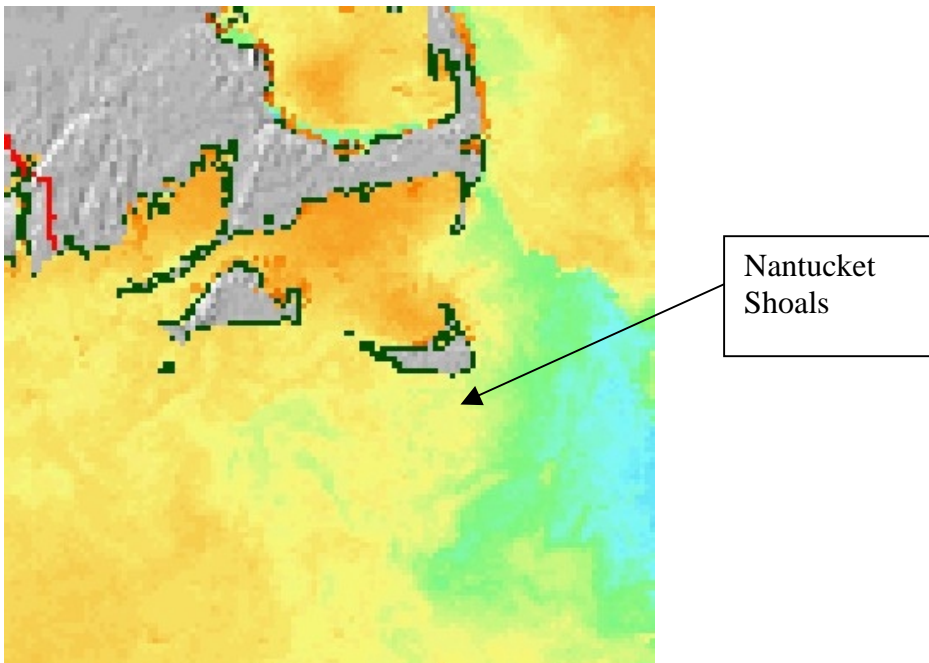


Figure 5 AVHRR sea surface temperature image for 1 August 2001. Warmest levels (orange) are 24 °C while coldest (blue) are 10 °C.

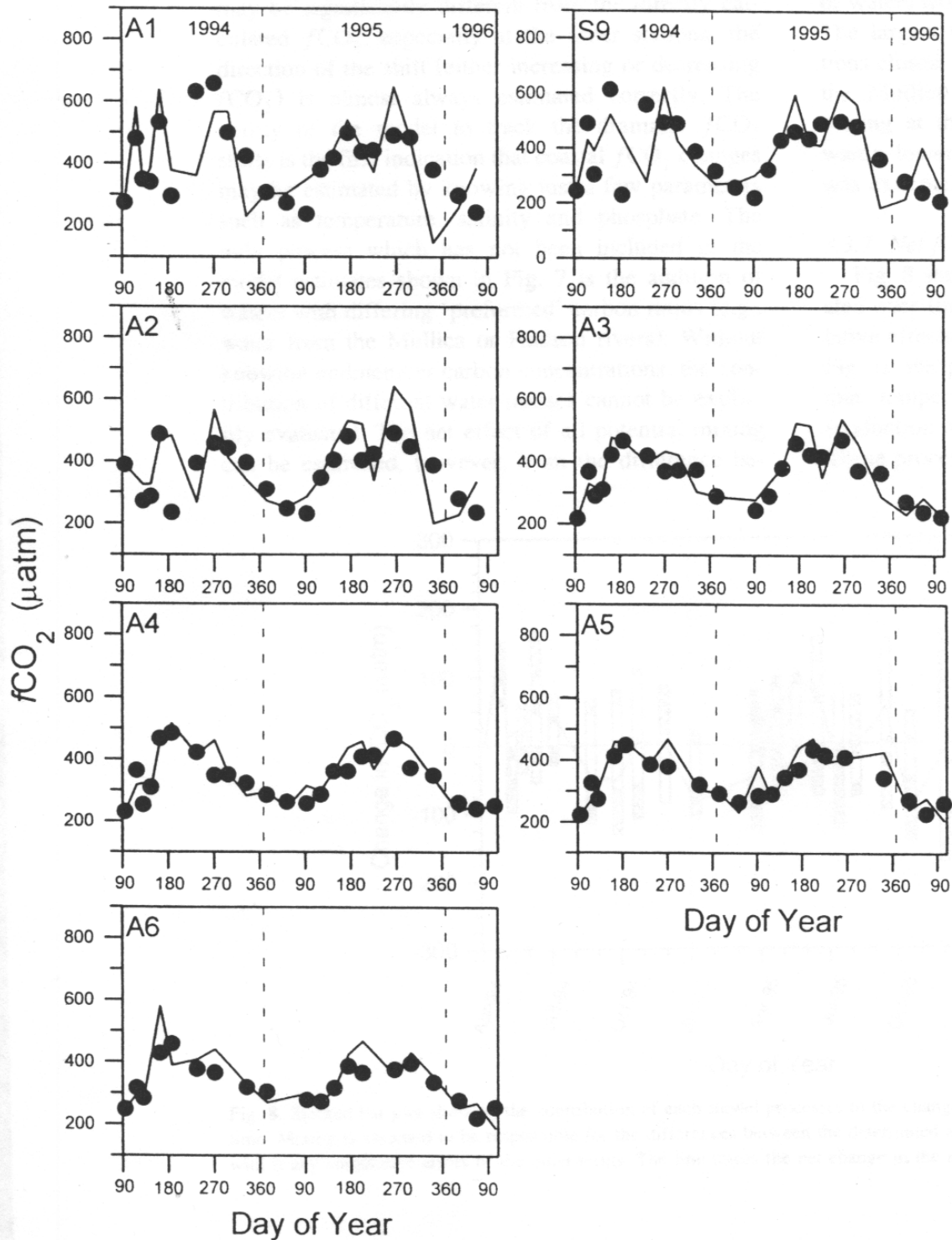


Figure 6 Time series $f\text{CO}_2$ observations from Boehme et al. (1998) (their Figure 7). The panels represent separate sampling stations from near shore (A1) to off shore (A6) where off shore is 22 km from the coast. Their multivariate regression (lines) and measured (filled circles) data are shown. Note that higher variance is observed near to the coast.

LDEO/CDIAC surface obs. within CBLAST region

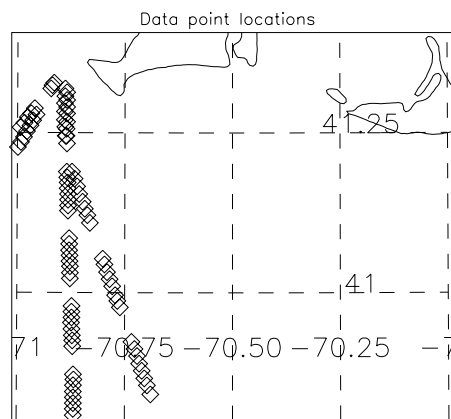
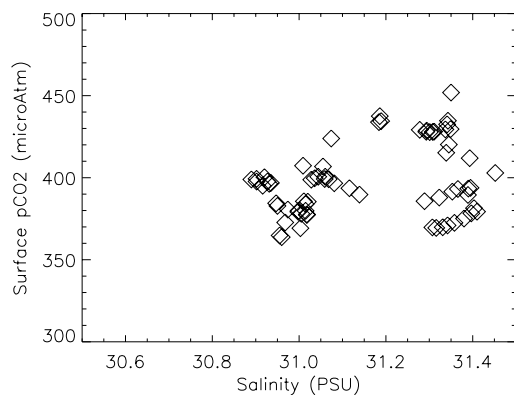
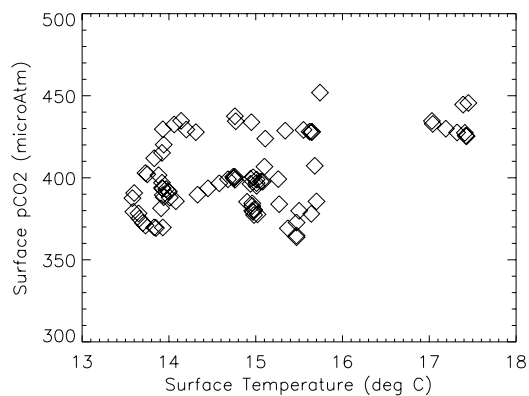
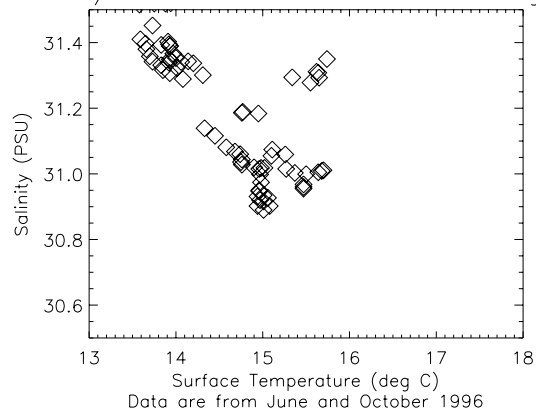


Figure 7 Data from 1996 OMP sea surface sampling program near to the CBLAST site. Sample locations are shown in the bottom panel. Top panel shows temperature and salinity, second panel show pCO₂ vs. temperature, and third panel shows pCO₂ vs. salinity. The data were collected in June and October of 1996.

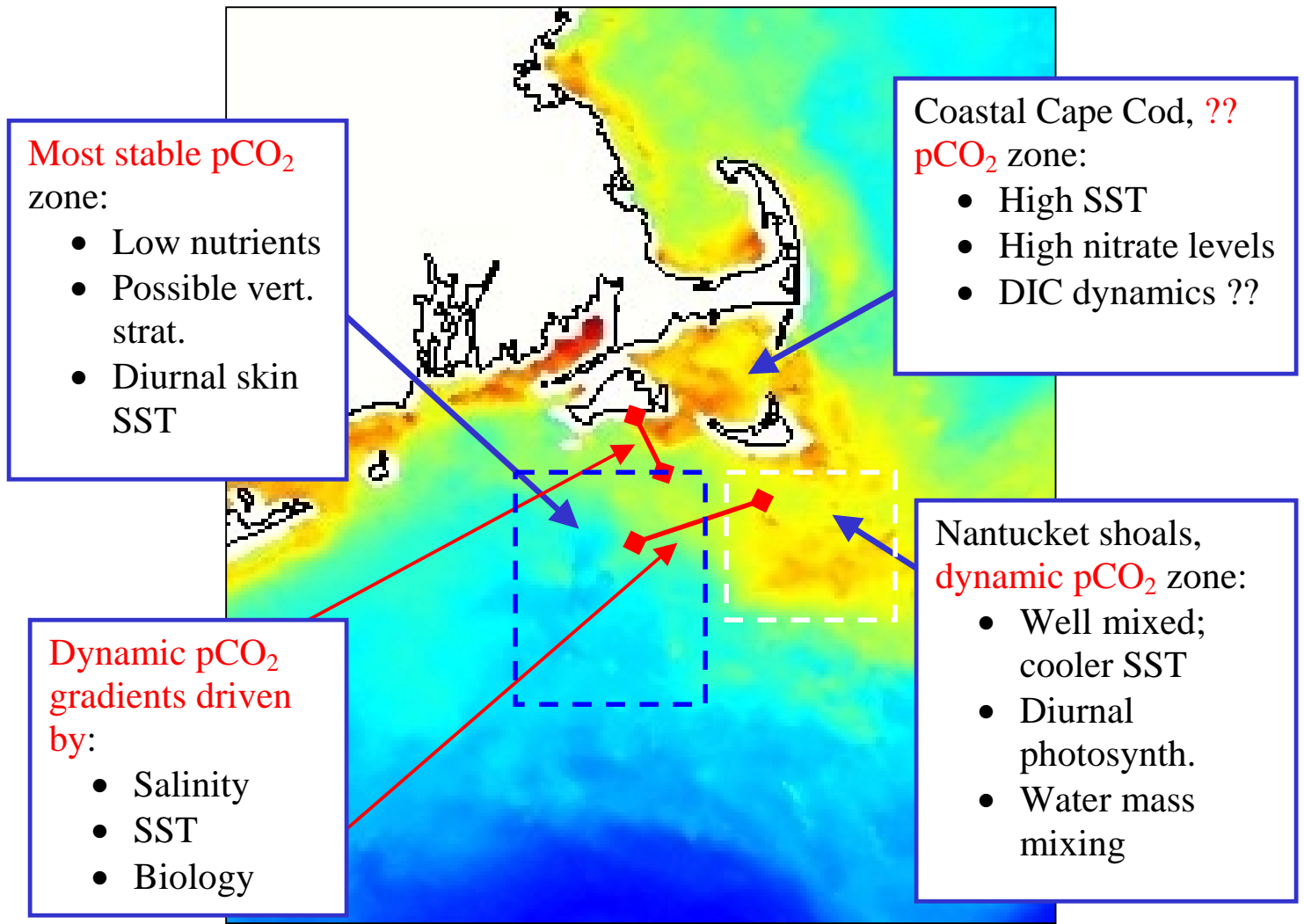


Figure 8 Schematic of the CBLAST region $p\text{CO}_2$ dynamics superposed on the SeaWiFS chlorophyll image.

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